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NRL Report 8397

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Catalytic Oxidation of Carbon Monoxide at High Humidity and Low Temperature

J. K. MUSICK AND F. W. WILLIAMS

*Combustion and Fuels Branch
Chemistry Division*

June 10, 1980



NAVAL RESEARCH LABORATORY
Washington, D.C.

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NRL Report 8397	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) CATALYTIC OXIDATION OF CARBON MONOXIDE AT HIGH HUMIDITY AND LOW TEMPERATURE		5. TYPE OF REPORT & PERIOD COVERED Interim report on a continuing NRL Problem
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) J. K. Musick and F. W. Williams		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Research Laboratory Washington, DC 20375		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 63561N; SO 205SL; 61C-07-13
11. CONTROLLING OFFICE NAME AND ADDRESS Department of the Navy Naval Sea Systems Command Washington, DC 20362		12. REPORT DATE June 10, 1980
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 18
		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Carbon monoxide Catalyst Hopcalite Palladium Low temperature		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Two catalysts (hopcalite and palladium) were tested for efficiency in promoting oxidation of carbon monoxide (CO). The catalysts were tested using air at $21\ 000\ h^{-1}$ space velocity, 50% relative humidity, and various temperatures. The air was contaminated with approximately 100 ppm each of methane, dichlorofluoromethane (R-12), and dichlorotetrafluoroethane (R-114) in addition to approximately 5000 ppm of CO. Hopcalite was further tested under similar conditions except that the air was at 100% relative humidity.		

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20. Abstract (Continued)

There is little difference in the efficiencies of hopcalite and palladium catalyst for oxidizing CO at 57 to 62°C; both are low. At 119 to 122°C, the palladium is more efficient than hopcalite. The simultaneous presence of three other contaminants decreased the efficiency of both hopcalite and palladium for oxidizing CO. With the hopcalite preheated to about 119°C, the heat of reaction is not sufficient to maintain the oxidation of CO under the conditions tested. The minimum temperature at which hopcalite and palladium catalysts will completely oxidize CO under the conditions tested is in the 70 to 100°C range.

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CATALYTIC OXIDATION OF CARBON MONOXIDE AT HIGH HUMIDITY AND LOW TEMPERATURE

INTRODUCTION

The work reported here is a continuation of that covered in NRL Report 8353 on catalytic oxidation of carbon monoxide at low temperatures [1]. As pointed out in that report, the Navy has a need for a method by which high concentrations of carbon monoxide (CO) can be removed from a submarine with the use of little or no electric power. The reason for this need is that in an emergency situation, such as a fire, it is quite possible that a ship could have a loss of or reduction in available electric power at the same time that its atmosphere was heavily contaminated with CO. The only method now available for removing CO from a vessel without the use of power is ventilation. Normally CO is removed from a submarine by passing the ship's air through a catalytic burner. In the burner, CO is oxidized to carbon dioxide (CO₂) by using hopcalite catalyst maintained at 316°C by electric heaters.

The burner operating temperature of 316°C was originally selected on the basis of results of experimental work. Tests have shown that water vapor in typical submarine air (approx. 50% relative humidity (R.H.)) completely destroys the activity of hopcalite for CO at room temperature [2]. At intermediate temperatures (between 100 and 300°C), it was found that hopcalite adsorbed organic compounds which could explode if the temperature of the catalyst were subsequently increased or cycled sufficiently [2]. Further, at these intermediate temperatures some chlorinated hydrocarbons were found to be converted to toxic compounds by the hopcalite [3]. Consequently, 316°C was chosen as the most practical temperature for operation of the burner.

In the previous work [1], the efficiencies of four different catalysts for converting CO to CO₂ in air at various temperatures and humidities were measured. These catalysts were: (a) Whetlerite, an impregnated carbon, (b) hopcalite, (c) palladium metal, and (d) platinum metal. The work covered by this present report, as originally planned, was to test three of these same catalysts further. Whetlerite showed little promise in the preliminary work and was not included in the present study. The plan was to test the three other catalysts under the same conditions used in the previous tests (in which CO was the only contaminant) but with the additional condition that the catalysts be simultaneously exposed to high concentrations of three other contaminants. Before these tests were completed, however, during a Program Review on 26 July 1979, the Naval Sea Systems Command (Code 05R) made an oral request to redirect the work. The new objectives were (a) to test the capability of hopcalite for oxidizing CO in air at 100% R.H. (measured at room temperature) and (b) to determine whether the heat of reaction would be sufficient to keep hopcalite oxidizing CO in 100% R.H.-air once the burner was brought to operating temperature by the use of electric power. Therefore, the work done and here reported consists

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of two phases: (a) measurement of the efficiencies of both hopcalite and palladium catalysts for oxidizing CO in the presence of three other contaminants in air at 50% R.H. and (b) measurement of the efficiency of hopcalite in oxidizing CO in the presence of three other contaminants in air at 100% R.H.

The ultimate objective of the work is to devise a method of reducing the CO concentration in a submarine atmosphere from 5000 to 50 ppm and maintaining it at 50 ppm for 72 h with a minimum or no use of electric power.

APPARATUS

A continuing series of studies of various problems associated with the CO/H₂ burner has been carried out at the Naval Research Laboratory since before the time of the launching of the first nuclear submarine. Most of these studies involved the use of a laboratory-scale catalytic burner designed to reproduce in a small catalyst bed the conditions that exist in the shipboard catalyst bed, such as contaminant concentrations, pressure, temperature, linear flow velocity, and residence time. The first four of these variables are readily adjustable in the laboratory burner and can be set to duplicate the conditions in the ship's burner. The fifth variable, residence time (of air in the catalyst bed), is dependent on both linear air velocity and the dimensions and characteristics of the catalyst bed. For this reason, the catalyst bed of the laboratory burner was made the same depth as that used in the shipboard burners. This ensured that when the linear air velocity of the shipboard burner was duplicated in the laboratory burner, the residence time was simultaneously duplicated, provided that both burners were loaded with the same catalyst.

The laboratory-scale burner (Fig. 1) is a reactor with an integral preheater both of which are contained in a 71-cm length of 2.9-cm stainless steel tubing mounted vertically and surrounded by two separate electrical heaters. The heaters are independently powered by two variable-voltage transformers, and the tube-heater assembly is heavily insulated with alumina-silicate fiber blanket and wrapped with glass tape. The upper section of the tube is packed with stainless steel turnings and serves as a preheater for the inlet air, and the lower section contains the catalyst bed. Two thermocouples are located in the burner tube: one is between the preheater and the catalyst bed and the other is at the exhaust end of the catalyst bed. The thermocouples are connected to a digital pyrometer that can be switched to display the temperature reading of either the catalyst bed inlet or exhaust air.

The burner is equipped with eight sampling lines of 0.3-cm o.d. stainless steel tubing to permit sampling of the air at the burner inlet, the preheater exhaust (between the preheater and catalyst bed), at 2.5-cm increments of catalyst bed depth, and at the burner exhaust. The bed-sampling tubes are welded to the burner tube and have 0.2-cm o.d. extensions with square-cut ends which project 1 cm into the catalyst bed. The inlet and exhaust sampling tubes are attached to the burner inlet and exhaust lines with tube fittings and do not project into the airstream. The sampling tubes are about 1.2 m long to provide cooling for the gas samples and are connected through stainless steel toggle valves to a gas chromatograph. These provisions for sampling and analyzing the burner airstream at successive 2.5-cm increments of catalyst bed depth make it possible to follow very closely the reactions which take place in the catalyst bed.

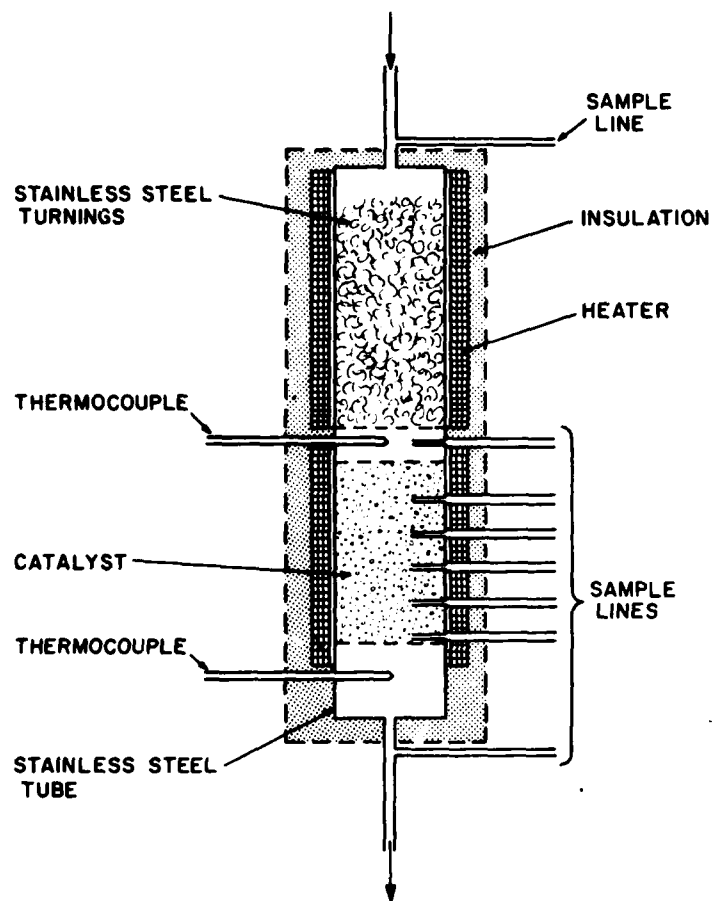


Fig. 1 — Laboratory-scale catalytic burner

The air supplied to the burner was taken from the laboratory 620 kPa (90-psi) air supply line and passed through a pressure regulator, needle valve, and flow meter for adjustment to the desired pressure and flow rate. In experiments using 50% R.H., the humidity was adjusted to that value by passing part of the airstream through a water bubbler at room temperature and then recombining and mixing it with the main stream. The humid air was then contaminated with the four compounds. The four contaminants were added by bleeding them from pressurized cylinders and controlling their rates of flow with small needle valves. These rates of flow were not measured but were adjusted to produce the desired concentrations as shown by the gas chromatography analyses. For three of the contaminants, pressure regulators were used to reduce and control the pressure applied to the needle valves. However, the vapor pressure of one contaminant (dichlorotetrafluoroethane) was low enough at room temperature to make it convenient to apply the cylinder pressure directly to the needle valve with no need for pressure reduction or regulation. The humidified

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contaminated air passed through a loop of 1/4-in. pipe, to mix it more thoroughly, and then to the burner inlet. A gate valve at the burner exhaust line was used to maintain a slight pressure on the burner to permit easy leak-free sampling of the burner air for analyses.

To produce air at 100% R.H., the apparatus was modified to the arrangement shown schematically in Fig. 2. In the modified apparatus, the entire airstream was passed successively through a bubbler warmed by an electric heating tape, a second bubbler in a controlled temperature bath, an entrainment trap, and a packed column. The trap and column were packed with 5/8-in. polypropylene Pall rings to remove entrained water droplets. The second bubbler was maintained at 33°C. This temperature was selected after several trials showed that it humidified the $4.7 \times 10^{-4} \text{ m}^3/\text{s}$ (1-cfm) airflow to 100% R.H. without producing an excessive amount of condensed water as the air cooled back to room temperature. The heating tape was used to keep the first bubbler warm to the touch as a matter of convenience. This reduced the use of water from the second bubbler and facilitated replenishing the supply. In a typical run, water did condense in the flow meter before the run was completed but none was detected in the apparatus at points farther downstream. In this apparatus, the second bubbler and the entrainment column were added because the existing bubbler and the trap used were too small. It was more convenient to add units which were available than it was to build new units of optimum size. Obviously, one bubbler and one trap could have been designed to do the job. As can be seen in Fig. 2, a bypass was provided so that dry air could be passed directly to the burner without being humidified. Also, there was provision to divert the airflow from the burner to a plastic bag in which the humidity could be measured.

CATALYSTS

The hopcalite was manufactured by the Mine Safety Appliances Corporation and was purchased through Navy supply channels on the military specification, MIL-C-21665 (Ships), 12 December 1958, amended 11 May 1959. It is a coprecipitate of copper and manganese oxides which has been analyzed as 78.3 wt-% MnO_2 and 13.1 wt-% CuO with a 7.9 wt-% ignition loss (presumably water or chemisorbed gases). The catalyst is about 6 mesh size and has an apparent density of 1 g/cm^3 .

The palladium catalyst is 0.5% palladium deposited on cylindrical alumina pellets 0.3 cm diameter \times 0.3 cm length and was manufactured by the Chemical Division of Englehard Industries, Inc.

CONTAMINANTS

In all the experiments, the burner air was contaminated with four compounds. All of these compounds are typical contaminants of submarine atmospheres but are present in submarines in much lower concentrations than those used in these experiments.

Carbon monoxide (CO) was used at a concentration of approximately 5000 ppm. Methane (CH_4), dichlorodifluoromethane (CCl_2F_2 or R-12), and dichlorotetrafluoroethane ($\text{CClF}_2\text{CClF}_2$ or R-114) were all used in concentrations of approximately 100 ppm. These

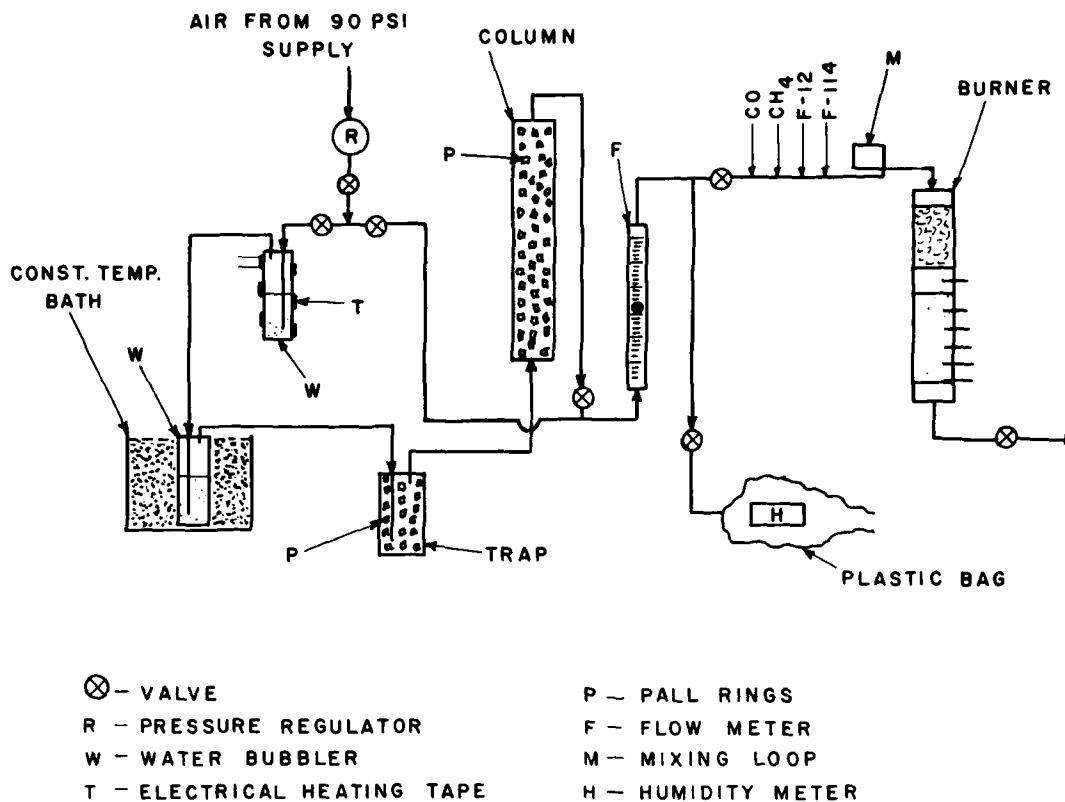


Fig. 2 - Modified apparatus for testing hopcalite at 100% R.H.

latter three contaminants are very resistant to catalytic decomposition but were added to determine whether their presence would affect the oxidation of the CO.

ANALYSES

The CO was analyzed with a Hewlett-Packard 5830A gas chromatograph using a thermal conductivity detector with a 180×0.6 cm stainless steel column of 70/80 mesh type 5A molecular sieve at 150°C .

The CH_4 , R-12, and R-114 were analyzed with the same gas chromatograph using a flame ionization detector with a 60×0.3 cm stainless steel column of 80/100 mesh Porapak S in tandem with a 150×0.3 cm stainless steel column of 80/100 mesh Porapak P at 150°C .

The humidity was measured by a Bendix 566 "Psychron" humidity meter which is basically two thermometers (wet bulb and dry bulb). To measure the humidity of an air-stream, the instrument is placed in a plastic bag through which the air is flowing. Identical wet and dry bulb temperatures indicate 100% R.H.

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PROCEDURE

The planned procedure was to measure the oxidation efficiencies of both hopcalite and palladium catalysts in the laboratory-scale burner under the following conditions:

- (1) Two temperature ranges; 52 to 66°C and 113 to 121°C
- (2) Inlet air contaminated with 5000 ppm of CO and 100 ppm each of CH₄, R-12, and R-114
- (3) Inlet air at 50% R.H.

Additionally, the hopcalite was to be tested with inlet air at 100% R.H.

As can be seen in Table 1, a certain amount of deviation from the planned conditions was accepted. This was done in order to minimize startup time and provide a longer run under equilibrium conditions. Measured concentrations in the burner inlet air varied from 4100 to 6600 ppm for the CO and from 74 to 137 ppm for the other contaminants. Tests were run at exhaust temperatures within or very near to the specified ranges, and a few additional tests were made at other temperatures. Exhaust temperatures are considered to be the burner temperatures since they are higher than inlet temperatures (due to the heat of reaction) and presumably are the controlling temperatures for the reactions. Temperatures, flow rates, and contaminant concentrations remained relatively constant throughout a day's run after equilibrium conditions were established.

To better simulate a real situation in which the CO concentration would decrease as burner operating time increased, the two catalysts were each given an additional test. In these, the burner was brought to equilibrium at standard operating conditions with the catalysts exposed to the four contaminants. After equilibrium was reached, burner power input, airflow rate, and contaminant flow rates (with the exception of CO) were not manually adjusted. The CO concentration was reduced in steps, while the visual measurements and analyses were made at successively lower CO concentrations throughout the run.

Only hopcalite was tested in air at 100% R.H. In these tests, the hopcalite was exposed to 6200 to 6600 ppm of CO simultaneously with 112 to 127 ppm of each of three contaminants (CH₄, R-12, and R-114) in air of 100% R.H. at 64 to 84°C. In addition to determining the oxidizing efficiency of hopcalite under these conditions, two tests were made to determine whether the heat of reaction was sufficient to sustain the oxidation of CO in 100% R.H.-air after the burner was preheated. These tests were run with the burner preheated to 59 and 119°C.

For the 100% R.H. tests, air measuring 95 to 100% R.H. on the "Psychron" was accepted as 100% R.H. or saturated air. Since some moisture from the humid airstream condensed before the air reached the burner, it appears that the humidity was as high as it is reasonably possible to obtain. A slight change in temperature of saturated air can cause either moisture to condense from the air or the relative humidity of the air to drop. For example, increasing the temperature of saturated air from 22 to 23°C decreases its relative humidity from 100 to 94%.

Table 1 — Summary of Results

Test No.	Av. Inlet Temp.		Av. Exh. Temp.		Inlet Contam. Conc. (ppm)				Proportion of Inlet CO Removed (%)	Proportion of Catalyst Bed Utilized (%)	Proportion of CO Oxidized by First Inch of Catalyst (%)
	(°F)	(°C)	(°F)	(°C)	CO	CH ₄	R-12	R-114			
Hopcalite with Inlet Air at 50% R.H.											
327 ^a	129	54	135	57	3500-5000	0	0	0	50	100	—
349	133	56	144	62	5100	110	90	97	33	100	—
353	221	105	252	122	4600	100	107	102	100	60	40
354	225	107	260-200	127-93	4300-0	93	74	84	100	—	—
Palladium with Inlet Air at 50% R.H.											
338 ^a	136	58	145	63	4300	0	0	0	26	100	—
356	135	57	135	57	4500	111	109	115	18	100	—
358	223	106	247	119	5000	115	113	102	100	40	69
360	215	102	300-185	149-85	5600-0	110	137	104	100	—	—
Hopcalite with Inlet Air at 100% R.H.											
361	140	60	151	66	6600	113	112	126	31	100	—
362	140	60	147	64	6200	112	112	122	28	100	—
362	149	65	184	84	6600	123	122	127	69	100	—
363	138-72	59-22	144-74	62-23	5600	104	98	95	6-0	100	—
364	244-72	118-22	274-79	134-26	5700	115	103	103	100-0	100	—

^aData from Ref. 1.

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In all the tests, an airflow of $4.7 \times 10^{-4} \text{ m}^3/\text{s}$ (1 cfm) was passed through the catalyst bed which has a 6.5-cm^2 cross-sectional area and a 12.7-cm depth. This provided a space velocity* of $21\,000 \text{ h}^{-1}$ which duplicates that of the shipboard catalyst bed.

Samples of burner air were taken at 2.5-cm increments of the catalyst bed depth and analyzed by gas chromatography. The analytical results for the CO were used to calculate catalyst efficiencies and contaminant decay rate curves to compare the characteristics of the catalysts. The other three contaminants are very resistant to catalytic decomposition, and analyses of the burner inlet and exhaust gases alone showed that no measurable quantities were oxidized.

RESULTS

Method of Presentation

The results are presented as curves which describe the performances the catalysts would provide if they were used in a full-size burner aboard a typical submarine. Each curve shows the decrease with time of the concentration of CO produced by the operation of one burner (using a particular catalyst and particular operating conditions) in a submarine atmosphere.

To determine the coordinates of these curves, the CO-removal efficiency of each catalyst studied was evaluated in the laboratory-scale catalytic burner described above. The efficiencies were expressed as fractions of the inlet CO concentrations oxidized by the catalyst beds. The conversion from measured laboratory performance of a catalyst to calculated shipboard performance was made by the use of an equation. In this equation,

$$\log C = 3.7 - \frac{tA}{698},$$

C is the concentration (ppm) of CO in the submarine's atmosphere,

t is the time (minutes) from the startup of the shipboard catalytic burner, and

A is the fraction of CO entering the burner which is oxidized by the burner (measured in the laboratory).

The equation is based on the assumptions that a submarine of 4250 m^3 of floodable volume is contaminated with 5000 ppm of CO and that a catalytic burner handling $0.24 \text{ m}^3/\text{s}$ of the submarine's air removes the fraction, A , of the CO entering the burner. Further assumptions made in the derivation of this equation are:

1. There is rapid and complete mixing of components in the submarine atmosphere.

*Space velocity is defined as the volume of air flowing through the catalyst per hour per volume of catalyst.

2. There is no interchange of gas between the submarine and the outside atmosphere.
3. There is no further generation of CO in the submarine. The equation is derived and discussed in Ref. 1.

The results of the laboratory tests are summarized in Table 1. These results are converted by the method described above to the theoretical shipboard performance curves shown in Figs. 3, 4, and 5.

Hopcalite Catalyst in 50% R.H.-Air

The performance of hopcalite in oxidizing CO in the presence of three other contaminants in air at 50% R.H. is shown in Table 1 and Fig. 3. Under the conditions listed in Table 1, hopcalite oxidized 33% of the influent CO at 62°C and 100% at 122°C. At the higher temperature, 40% of the influent CO was oxidized by a 2.5-mm thickness of the catalyst bed. Test No. 354 was run to simulate the situation in which the CO concentration in the burner influent decreases continuously. In this test, the influent CO concentration was reduced, in steps, from 4300 to 0 ppm over a period of about 7-1/2 h. Power input and other operating conditions were not changed. Under these conditions, the exhaust temperature dropped from 127 to 93°C. The inlet temperature of about 107°C was not affected, and the efficiency of the burner for the removal of CO remained at 100%.

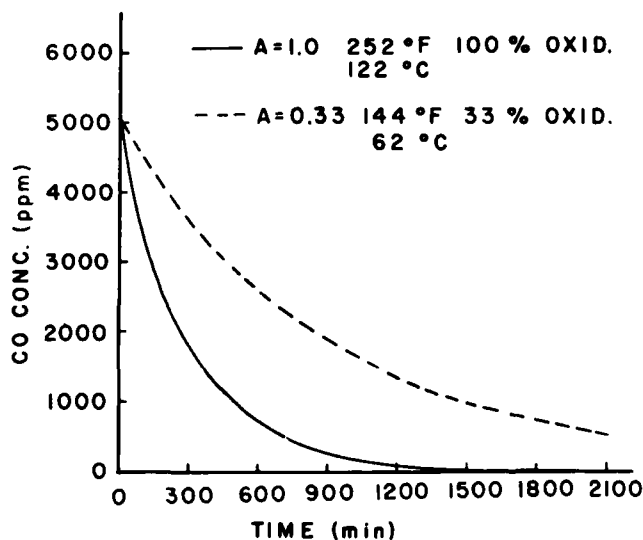


Fig. 3 — Performance of hopcalite—
Decrease in concentration of CO with
time, at 62 and 122°C and 50% R.H.

Palladium Catalyst in 50% R.H.-Air

Results of the tests of palladium catalyst are summarized in Table 1 and the CO-decay curves based on those data are shown in Fig. 4. The data show that 18% of the influent CO was oxidized by the palladium at 57°C and 100% at 119°C. At 119°C, 69% of the influent CO was oxidized by the first inch of the catalyst bed.

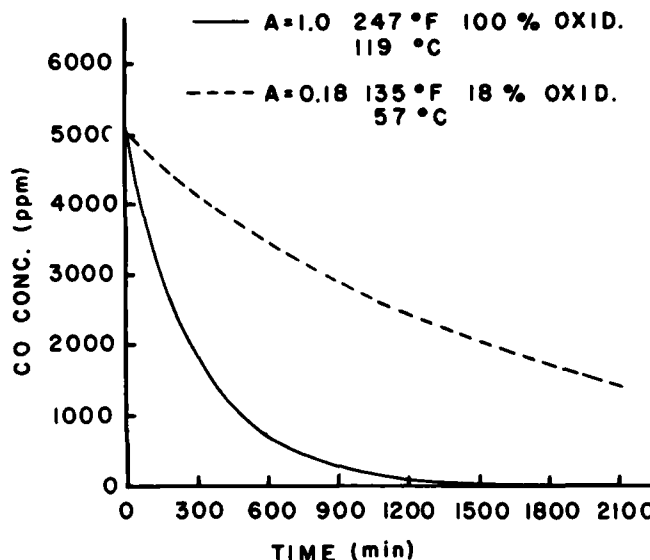


Fig. 4 — Performance of palladium—
Decrease in concentration of CO
with time, at 57 and 119°C and
50% R.H.

In test No. 360, the influent CO concentration was reduced, stepwise, from 5600 to 0 ppm during a period of more than 6 h while the other operating conditions were not changed. As a result, the burner exhaust temperature dropped from 149 to 85°C during the run. The burner inlet temperature remained constant and the burner continued to oxidize 100% of the influent CO throughout the test.

Hopcalite Catalyst in 100% R.H.-Air

The results of tests of hopcalite in 100% R.H.-air are summarized in Table 1 and Figs. 5 and 6. In Fig. 5, the CO-decay curves for three of the tests tabulated in Table 1 are plotted. These data show that 28% of the influent CO was oxidized at 64°C, 31% at 66°C, and 69% at 84°C. A curve showing the rate of decay of CO concentration for 100% oxidation in the burner is included in Fig. 5 for reference.

In two tests (Nos. 363 and 364), the burner was brought to test temperature using humidified, uncontaminated air. At that point, the contaminants were admitted to the burner inlet air and the power supply was cut off. Following this, no further adjustment of

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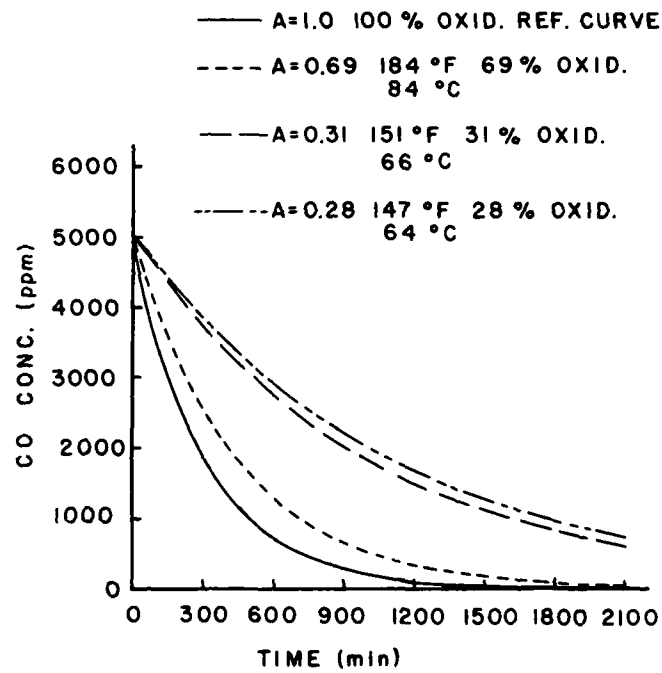


Fig. 5 — Performance of hopcalite—Decrease in concentration of CO with time, at various temperatures and 100% R.H.

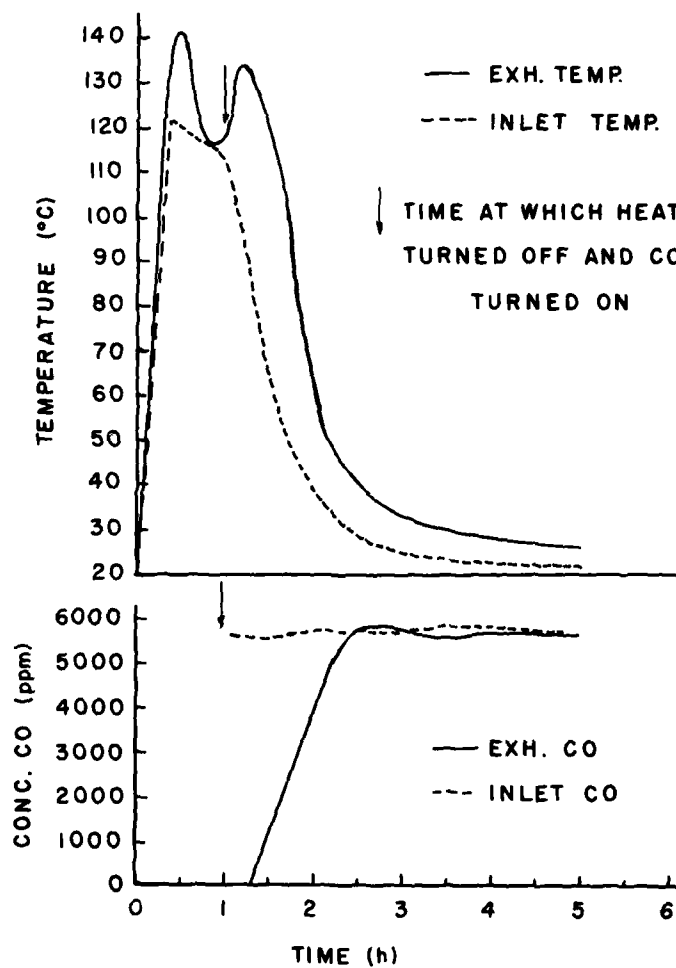


Fig. 6 — Performance of hopcalite—Effect of heat of reaction on burner temperature

the burner controls was made while the temperature and CO concentration of the burner inlet and exhaust air were measured at intervals throughout the run. In test No. 363, the power was turned off when both inlet and exhaust temperatures were at 59°C at which point the CO was introduced. The heat of reaction immediately raised the exhaust temperature to 62°C but within about 1 h it had dropped to 32°C. At first, the hopcalite oxidized 6% of the 5600 ppm of influent CO but within about half an hour no CO was being oxidized.

In Fig. 6, the temperatures and CO concentrations for test No. 364 are plotted. The power was turned off and the contaminants turned on with the burner at 119°C. The heat of reaction increased the burner exhaust temperature to 134°, after which it fell rapidly to room temperature. The burner oxidized all of the CO in the influent air for 1-1/4 h. After about 1-1/2 h, all of the influent CO passed through the burner unoxidized.

DISCUSSION

To determine whether the presence of the three additional contaminants (CH₄, R-12, and R-114) affects the performance of the hopcalite, it is necessary to compare the data of this report with that of the previous report [1]. For this reason, two tests from the previous report are included in Table 1. By comparing test No. 327 with test No. 349, it appears that the presence of the three additional contaminants may have had a small effect on the efficiency of the hopcalite. In the presence of CH₄, R-12, and R-114, the hopcalite oxidized about 33% of the influent CO at 62°C. With no additional contaminants present, the hopcalite oxidized about 50% of the influent CO at the lower temperature of 57°C.

A similar comparison of tests Nos. 338 and 356 in Table 1 can be made for the palladium catalyst. In the presence of the three additional contaminants (test No. 356), it is seen that the palladium oxidizes 18% of the influent CO at 57°C. With no additional contaminants present (test No. 338), the palladium oxidized 26% of the influent CO at 63°C. Here also, the presence of the three additional contaminants appears to have slightly lowered the activity of the catalyst for CO.

There appears to be little difference between the performance of hopcalite and that of palladium at the lowest temperature tested. The palladium (test No. 356) oxidized 18% of the influent CO at 57°C while the hopcalite (test No. 349) oxidized 33% at 62°C. However, the palladium is more efficient at higher temperature. By comparing tests No. 358 and 353, it is seen that 2.5 cm of the palladium catalyst bed oxidizes 69% of the influent CO at 119°C, while a similar thickness of the hopcalite bed oxidizes only 40% of the CO at 122°C.

Comparing test No. 349 with tests Nos. 361 and 362 shows that hopcalite was slightly more efficient in the 50% R.H.-air than it was in the 100% R.H.-air. However, the improvement is small and could be due to normal scattering of the data rather than to any real improvement in performance of the catalyst.

Plots of the percentages of the influent CO oxidized by 2.5-cm-thick beds of the two catalysts at different temperatures and humidities are presented in Fig. 7. It has been shown (see Figs. 8 and 11 of Reference 1) that, in the range of concentration with which we are

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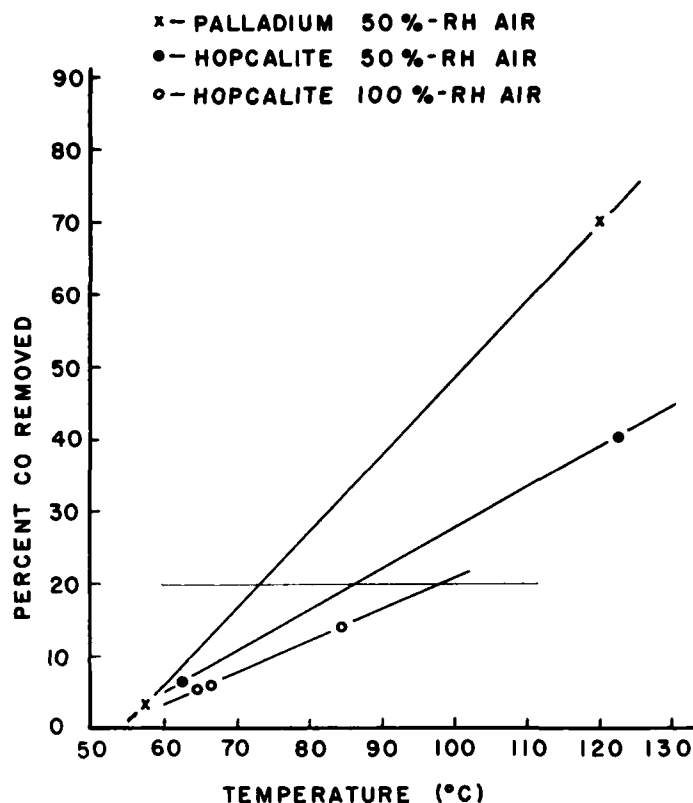


Fig. 7 — Percent of influent CO oxidized by a 2.5-cm layer of catalyst vs temperature

here concerned, equal increments of the catalyst bed oxidize equal proportions of the contaminants. Therefore, the points at which the plotted lines in Fig. 7 intersect the 20%-removal line indicate the minimum temperatures at which the catalysts will oxidize 100% of the influent CO (since at this point 20% of the catalyst bed is removing 20% of the influent CO). Additional data are needed to determine these temperatures more accurately, but on the basis of the present information, these temperatures are between 70 and 100°C for all three conditions (palladium in 50% R.H.-air, hopcalite in 50% R.H.-air, and hopcalite in 100% R.H.-air).

CONCLUSIONS

1. The simultaneous presence of 100 ppm each of CH₄, R-12, and R-114 decreases the activity of both hopcalite and palladium for CO (tested with 5000 ppm of CO in air at 50% R.H.).

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2. There is little difference in the efficiencies of hopcalite and palladium catalyst for oxidizing CO in air at 50% R.H. and 57 to 62°C. At 119 to 122°C, however, the palladium is more efficient than hopcalite.

3. At 119°C, the heat of reaction is not sufficient to maintain the oxidation of 5000 ppm of CO by hopcalite catalyst in air contaminated with 100 ppm each of CH₄, R-12, and R-114 and at 100% R.H.

4. The minimum temperature at which hopcalite will completely oxidize 5000 ppm of influent CO in 100% R.H.-air and in the presence of 100 ppm each of CH₄, R-12, and R-114 is between 70 and 100°C. This is also true for both hopcalite and palladium catalysts in 50% R.H.-air.

ACKNOWLEDGMENT

The authors are indebted to Mr. Harold G. Eaton of the Combustion and Fuels Branch, Chemistry Division, Naval Research Laboratory, for his help in devising analytical procedures and solving gas chromatograph problems.

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